## Supercritical fluid controls on mantle $f_{O_2}$ with diamond and carbonic acid

## D. A. SVERJENSKY

Johns Hopkins University, Baltimore, MD 21218, USA (sver@jhu.edu)

Fluids in the mantle can no longer be regarded as simple molecular COH fluids. Abundant evidence from fluid inclusions in diamonds and experimental studies of eclogite and peridotite solubilities demonstrate the complex solute chemistry of mantle fluids [1 - 3]. Recent advances in modelling deep Earth fluids by calibrating with high pressure and temperature rock solubilities referring to subsolidus conditions [4] now enable modelling of supercritical fluids.



A key aqueous species at pressures between 3.0 and 10.0 GPa is carbonic acid:  $H_2CO_3$  - a molecule that geochemists have long forgotten [5].  $CO_2$  is unimportant in high pressure fluids. Instead, the  $f_{O_2}$  of fluids in equilibrium with diamond is controlled by redox equilibria in the fluid between inorganic and organic C-species with high molalities:

e.g. 
$$H_2CO_3^0 = HCOO^- + H^+ + 0.5O_{2,g}$$
  
and  $C(+|V) = C(+|I|)$   
 $2HCOO^- + 2H^+ = C + H_2CO_3^0 + H_2O_{C(+|V)}$ 

The above reactions model the control of  $f_{O_2}$  measured in a fluid in equilibrium with a mafic eclogite at QFM - 2.7 [6], without any significant methane in the fluid. In summary, inorganic and organic metal complexes give high solubilities in mantle fluids with complex chemistry. Modelling of supercritical mantle fluids can now proceed from water-rich to silicate-rich fluid compositions. The high concentrations of C-species such as  $H_2CO_3$  and  $HCOO^2$  can control the  $f_{O_2}$ during the fluid-rock interactions involved in mantle metasomatism and diamond formation.

[1] Weiss et al. (2015) Nature 524, 339-342. [2] Kessel et al. (2005) EPSL 237, 873-892. [3] Kessel et al. (2015) CMP 169, 37-56. [4] Huang & Sverjensky (2019) GCA, in press.
[5] Pan & Galli (2016) Sci. Adv. 2, e1601278. [6] Elazar et al. (2019) GCA, in press.